

## Synchrotron X-Ray Study of Ethylene-propylene Elastomer Under Deformation

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Beamline: X27C

**Introduction:** The studies [1-2] of ethylene-propylene (EP) random copolymers under deformation are closely related to many industrial applications and are of significant academic interests. For example, the molecular organization in the crystalline phase of oriented ethylene-propylene random copolymer has been studied with X-ray diffraction by de Ballesteros [1]. It has been noted that the use of WAXD alone cannot reveal the full picture of the structure and morphology changes. To better understand the development of structure and morphology under deformation, one needs to combine small-angle X-ray scattering (SAXS) experiment (which probes the polymer lamellar morphology) with wide-angle X-ray diffraction (WAXD) experiment. In the present work, simultaneous synchrotron SAXS and WAXD techniques were carried out to investigate an EP copolymer with 78 wt% of ethylene within the elongation ratios from 50 to 600 %. Our results provide a full picture about the changes in structure and morphology of the EP copolymer at both molecular and lamellar levels during the stretching process.

**Methods and Materials:** Ethylene-Propylene copolymer with 78 wt % of ethylene was provided by ExxonMobile Chemical Company. The molecular weight of the sample is  $M_w = 153,000$ . Samples were melt pressed at  $180^\circ\text{C}$  into thin films (width, thickness and length of 5 mm, 1 mm, 5 mm, respectively) for X-ray studies. An Instron 4400 tensile apparatus was used for deformation study with a stretching speed 5 mm/min. All deformation experiments were carried out at room temperature. Simultaneous WAXD and SAXS measurements during deformation were carried out at the X27C Beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength used was 0.1366 nm. Two Fuji imaging plates were used to collect the *in-situ* SAXS and WAXD images during deformation. The imaging plate used for WAXD had an opening in the center, allowing the passage of the SAXS signals. The sample-to-detector distance for the present WAXD and SAXS study was 164 mm and 1211mm, respectively. The WAXD profiles were calibrated with the silicon standard, while SAXS profiles were calibrated with silver behenate.

**Results:** The copolymer showed a homogenous scattering ring (in SAXS) with a d-spacing about 21 nm with 0% elongation, as illustrated in Fig 1. This d-spacing corresponded to the average long period of the randomly organized crystalline ethylene lamellar stacks. When the elongation rate was 50%, the scattering ring was split into four scattering arcs, implying ethylene lamellar stacks were partially oriented into a superstructure. Further increasing elongation ratio to 100%, the scattering arcs changed into four scattering spots, suggesting an improved orientation but still having a unique tilted molecular orientation in the superstructure. When the elongation ratio reached to 150%, an oriented scattering pattern with two meridional scattering arcs was seen. The scattering profiles in stretching direction are shown in Fig 2. The decrease in the peak intensity in Fig 2 for elongation ratios 50% and 100% were due to the four arcs scattering feature as shown in Fig 1, instead of suggesting a real change in the d-spacing of the lamellar stacks. A very oriented scattering pattern with only two scattering bars was seen when the elongation ratio was 200% or higher, indicating that the ethylene crystals were highly oriented when the elongation ratio reached 200%. The profiles (Fig 2) with elongation ratios equal to or larger than 200% also show that once the crystals were well oriented (two meridional scattering bars), the average long period of the oriented crystals increased with increasing elongation ratio.

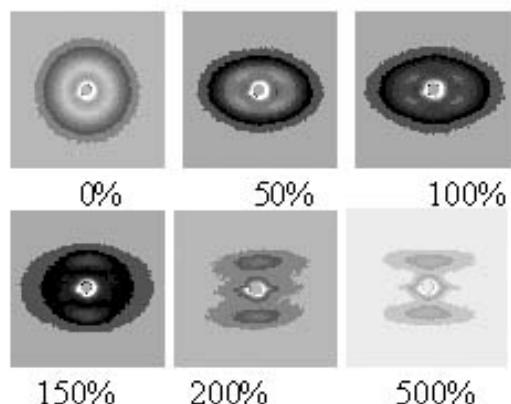
The information on crystal and polymer chain orientation can also be obtained from WAXD diffraction pattern. As shown in Fig 3, with an elongation ratio=50%, the ethylene crystals were highly oriented. Sharp diffraction arcs occurred in equatorial direction (vertical to stretching direction), suggesting a good orientation of the crystals. With an increase in the elongation ratio, the crystals were better oriented in the stretching direction and showed a strong diffraction intensity, as seen in Fig 3. From the diffraction profiles in the equatorial direction, it can be seen that when the elongation ratio was low (within 100%), the intensity of crystalline diffraction peak was relatively low, and the amorphous halo was relatively large. With increasing the elongation ratio, the amorphous chains were also oriented well, so that only a single sharp diffraction/scattering peak was seen. The single diffraction peak indicating that the ethylene crystal structure in the EP copolymer has a pseudo -hexagonal packing, instead of the well known orthorhombic habit. The SAXS images in Fig 5 show the change in the SAXS pattern from a very high elongation ratio relaxes to a lower one. It is seen that if the sample is directly stretched to an elongation ratio of 400%, a SAXS scattering pattern with only two meridional bars is seen (Fig 1). However, when the sample was stretched to 600% than relaxed to 400% (Fig 5), a SAXS pattern with a four scattering spots was observed. The pattern in Fig 5(c) is similar to the one in Fig 1 with an elongation ratio 150%. The pattern in Fig 5(c) suggests that: (1). the crystal domains became less oriented when the sample was relaxed back to a lower elongation ratio; (2). the orientation-induced crystallization might make a reversible structural change impossible.

**Conclusions:** By combining the SAXS and WAXD data, the following conclusions can be made: (1). the crystalline structure and crystal orientation changes appreciably with elongation from 0 to 200%; (2). when elongation is larger than 200%, ethylene domains are completely aligned in the stretching direction, and the chains in the crystal domains are also aligned in the stretching direction; (3). when elongation is larger than 200%, the polymer chains in the amorphous region are also highly oriented with orientation induced crystallization possibly occurring.

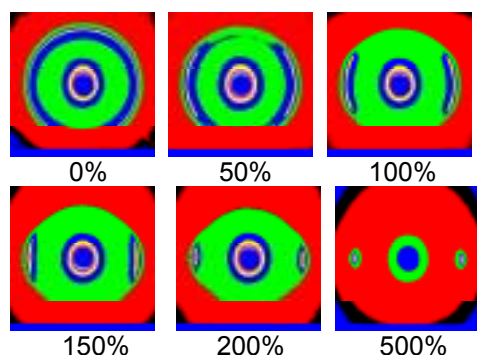
**Acknowledgments:** This work was support by NSF (DMR-0098104).

**References:** 1. de Ballesteros, O.R; Auriemma, F.; Guerra, G.; Corradini, P. *Macromolecules* **1996**, 29(22), 7141.

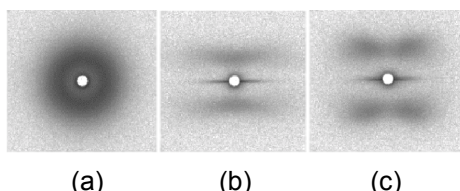
2. Kolbert, A.C.; Didier, J.G.; Xu, L. *Macromolecules* **1996**, *Macromolecules* **1996**, 29(27), 8591.



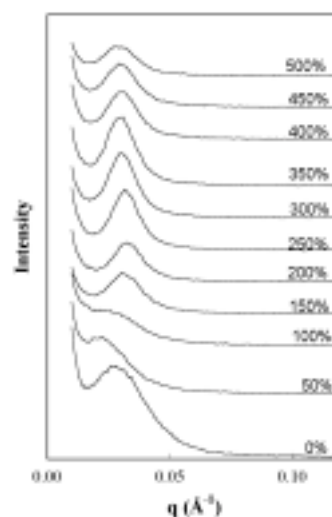
**Figure 1.** SAXS scattering images of the EP copolymer with different elongation ratios.



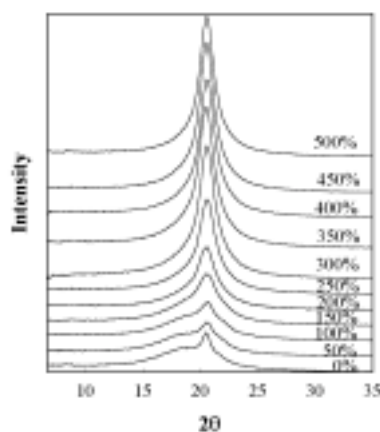
**Figure 3.** WAXD diffraction images of the EP elastomer with different elongation ratios.



**Figure 5.** SAXS scattering images of S3 copolymer. (a) no deformation; (b) elongation ratio=600%; (c) relaxed to an elongation ratio 400% from an elongation 600%.



**Figure 2.** SAXS scattering profiles in stretching direction of the copolymer with different elongation ratios.



**Figure 4.** WAXD diffraction profiles in equatorial direction (vertical to stretching direction) of S3 copolymer with different elongation